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The Content of Trace Metals (Cd, Cr, Cu, Ni, Pb, Zn) in Selected Plant Species (Moss *Pleurozium Schreberi*, Dandelion *Taraxacum Officianale*, Spruce *Picea Abies*) along the Road Cracow – Zakopane**

1. Introduction

One of anthropogenic sources of metals in the environment is traffic. Motor transport negatively influences the environment deteriorating air quality, polluting the soil and plants, ground waters, and surface waters, taking the land for the road infrastructure and exposing many people on noise above the acceptable level. Nowadays, we know 21 basic substances defined as toxic, and emitted by motor vehicles [1]. They include (among others) the following trace metals: Cd, Cu, Pb, Sb and Zn. Traffic pollutes the environment with different wastes such as: used car shells and tires, exploitation wastes, including oils, electrolytes, cooling liquids and materials used for washing and maintenance of vehicles.

Metal deposition, among others, depends on: the amount of emission, physical properties of the suspended particles, meteorological conditions, characteristics of soils and plants, including: plant species, surface of leaves and their morphology [2]. The presence of trace metals in the components of the environment makes the indicator of anthropogenic pressure. Thus, in the monitoring, stress is put on the determination of the level of accumulated metals in soil, plant and animals. The basic method of the monitoring studies is bioindication, including phytoindication.

In the studies of phytoindication certain plant species are used, called proper indicators and accumulators, characterised by specific features, related to indication. Many plant species possess the ability to absorb and accumulate potentially toxic substances. Particularly valuable are species possessing special abilities to accumulate a certain type of pollutants – so called phytoaccumulators [3].

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Mosses and lichens are considered to be very sensitive bioindicators of atmospheric pollution. Some moss species, especially *Pleurozium schreberi* and *Hylocomium splendens,* are widely applied bioindicators, because they show features of good accumulators (including the lack of cuticle and epidermis) and have a wide geographic distribution [4–6]. Also, some common vascular plant species are used in biomonitoring, although they accumulate trace elements less intensively compared to mosses and lichens. A good example is the dandelion *Taraxacum officinale*, used in many monitoring surveys carried out near the roads [7, 8]. Commonly used bioaccumulators are coniferous trees, including: the Norway spruce – *Picea abies* [9–12]. The basic factors making spruce – *Picea abies* suitable for monitoring survey are: easiness to assimilate atmospheric emission of heavy metals and sulphur, wide geographic distribution, occurrence in different habitats, annual growths of needles allowing the registration of changes in time.

2. Material and Methods

The studies were carried out in the vicinity of the road Cracow – Zakopane no. DK7 (Cracow – Zabornia) and no. DK 47 (Zabornia – Zakopane). The plant material was taken within seven transects perpendicular to the road (Głogoczów, Pcim, Tenczyn, Krzeczów, Skomielna Biała, Rdzawka II, Biały Dunajec) in four distances from the verge of the road: 5 m, 10 m, 50 m and 100 m. Moreover, in the following locations: the nature reserve "Las Bronaczowa", the hills of Bukowiec, Barnasiówka, Chełm, Łysina, Szczebel, Mały Luboń, Birtalowa, the mountain chain Stare Wierchy, and the nature reserve "Bór na Czerwonem", reference samples were taken for the mentioned above transects. The reference points were located in the minimum distance of 500 m from the road Cracow – Zakopane, far from buildings and local roads. Within every point 4–6 single samples of plants were taken and the mean result was calculated. For the phytoindication survey the following type plant samples: green segments of moss *Pleurozium schreberi* (Brid.) Mitt., representing growth within the latest 2–3 years; leaves of dandelion *Taraxacum officinale F.* H. Wigg. and two years old needles of spruce *Picea abies* (L.). The samples were taken in September 2006. The plant material was dried at 60°C. The grinded, air-dry material was mineralized in a mixture of concentrated acids: HNO_3 and $HClO_4$ in the proportion 4:1. General contents of Cd, Cr, Cu, Ni, Pb and Zn were determined using the ASA method of the spectrophotometer Hitachi model Z-8200.

3. Results and Discussion

The concentrations of trace metals in the analysed plant species, depending on the distance from the road and mean concentrations for all the localizations are presented in table 1.

Table 1. Trace metal concentrations in plants [μg/g d.w], mean values ($\bar{x}$), standard deviation (SD), and minimum–maximum values

Species	Distance from the road [m]	Metal, mean values $\bar{x}$ [μg/g d.w.] ±SD min – max values					
		Cr	Ni	Cu	Zn	Cd	Pb
Moss *Pleurozium schreberi*	5 n = 3	36.3±21.5 11.6–51.3	22.7±10.6 10.5–30.0	23.0±5.5 18.9–29.3	114.7±56.7 78.6–180.1	0.8±0.4 0.4–1.2	23.1±8.6 17.4–33.0
	10 n = 3	10.2±1.1 9.5–11.5	10.4±4.7 7.3–15.8	13.5±6.6 9.3–21.1	107.9±21.9 86.3–130.0	1.6±0.5 1.2–2.2	31.0±20.5 18.4–54.7
	50 n = 4	11.3±8.4 5.7–23.8	7.6±2.4 5.3–10.8	9.2±3.0 5.5–12.4	81.6±6.6 76.0–90.9	1.8±0.7 1.4–2.8	26.7±14.3 13.8–39.8
	100 n = 4	8.1±2.1 5.3–10.0	5.3±0.9 4.5–6.5	8.3±2.3 6.0–11.5	59.2±13.5 44.3–77.0	0.9±0.4 0.5–1.4	22.1±5.2 14.5–26.3
	Reference sample n = 3	9.6±4.5 4.4–16.8	7.0±4.0 2.1–14.3	10.5±2.9 6.0–13.5	70.6±30.6 30.9–120.9	1.6±1.0 0.4–3.3	23.1±14.7 7.4–48.7
Mean n = 17		13.1±11.4 4.4–51.3	9.0±6.8 2.1–30.0	11.6±5.0 5.5–24.1	79.6±27.0 30.9–129.4	1.5±0.8 0.4–3.3	24.2±10.9 7.4–48.7
Dandelion *Taraxacum officinale*	5 n = 9	6.2±3.7 2.0–14.5	3.4±1.7 0.8–6.2	14.8±3.0 0.8–20.5	52.1±13.7 31.1–81.5	0.5±0.5 0.2–1.7	3.9±1.8 1.3–6.0
	10 n = 9	3.2±2.0 1.3–6.2	2.9±1.9 0.3–5.8	14.2±2.7 10.5–18.7	45.8±24.5 25.3–106.0	0.9±1.2 0.1–4.0	1.7±1.3 0.3–4.3
	50 n = 9	1.9±0.9 1.0–3.0	2.9±2.1 0.5–7.0	17.8±17.2 8.5–63.3	41.2±14.0 24.0–67.0	1.1±0.6 0.3–2.0	2.0±1.4 0.3–4.3
	100 n = 9	1.8±1.2 1.0–5.0	5.0±2.9 2.0–10.3	12.5±1.6 9.5–14.8	44.7±10.9 27.1–60.5	2.1±1.4 0.6–4.5	2.2±1.8 0.3–5.5
	Reference sample n = 7	2.7±0.9 1.6–4.6	8.1±4.1 4.0–14.4	15.1±1.1 13.5–17.0	61.4±17.3 33.7–81.7	3.7±1.5 1.7–6.1	1.7±0.4 1.0–2.3
Mean n = 35		3.0±2.6 0.9–14.5	4.6±3.3 0.3–14.4	14.4±4.6 8.5–37.2	49.5±17.8 24.0–106.0	1.7±1.6 0.1–6.1	3.3±6.5 0.3–39.8
Spruce *Picea abies*	5 n = 9	2.3±1.8 0.5–6.8	1.7±1.3 0.1–4.3	4.4±2.6 2.3–10.3	48.2±11.4 29.3–64.8	0.3±0.7 0.1–2.1	2.7±2.6 0.3–7.3
	10 n = 9	1.6±0.6 0.5–2.5	2.5±1.5 1.3–6.0	2.9±0.9 1.0–4.0	51.8±22.6 18.7–82.3	0.2±0.2 0.1–0.6	2.1±1.2 0.5–4.0
	50 n = 9	0.9±0.4 0.3–1.5	2.2±1.6 0.1–4.3	2.3±0.7 1.5–3.8	37.4±11.5 15.7–48.8	0.2±0.1 0.1–0.4	1.8±1.6 0.1–4.8
	100 n = 9	1.2±0.4 0.8–1.8	2.3±1.7 0.5–6.3	2.2±0.4 1.5–2.5	44.1±16.7 21.1–80.0	0.3±0.2 0.1–0.6	2.6±2.4 0.3–7.3
	Reference sample n = 7	1.4±0.6 0.7–2.3	3.3±1.1 1.5–4.8	2.8±0.3 2.5–3.2	33.4±11.4 17.5–50.4	0.2±0.1 0.1–0.4	1.3±0.6 0.1–1.9
Mean n = 35		1.5±1.1 0.3–6.8	2.4±1.5 0.1–6.3	3.0±1.6 1.0–10.3	43.1±15.9 17.5–82.1	0.3±0.3 0.1–2.1	2.0±1.7 0.1–7.3

n – the number of measurements in the sample.

Coefficients of the enrichment of the plant material in metals, near the roads is presented in table 2. They are expressed as ratios of metal concentration in a specific distances from the road and the concentration in reference areas.

Table 2. Coefficients of the enrichment of plants in trace metals in specific distances from the road, in the relation to reference areas

Sample type	Coefficient	Cr	Ni	Cu	Zn	Cd	Pb
Moss *Pleurozium schreberii* $n = 3$	5/background	3.5	3.1	2.0	1.5	0.5	1.0
	10/background	1.0	1.4	1.2	1.4	0.9	1.3
	50/background	1.1	1.0	0.8	1.1	1.1	1.1
	100/background	0.8	0.7	0.7	0.8	0.5	0.9
Dandelion *Taraxacum officinale* $n = 9$	5/background	2.2	0.4	1.0	0.8	0.2	2.3
	10/background	1.1	0.4	0.9	0.7	0.3	1.0
	50/background	0.7	0.4	1.1	0.6	0.3	1.3
	100/background	0.7	0.6	0.8	0.7	0.6	1.3
Spruce *Picea abies* $n = 9$	5/background	1.4	0.5	1.6	1.6	1.8	2.3
	10/background	1.0	0.7	1.0	1.7	1.0	1.8
	50/background	0.6	0.6	0.8	1.2	1.1	1.5
	100/background	0.7	0.6	0.8	1.5	1.4	2.2

n – the number of samples.

Among the tested plants, the highest amounts of trace metals were accumulated by the moss *Pleurozium schreberi.* Its highest concentrations of Cr, Ni, Cu, Zn were found in the direct vicinity of the road (5 m, 10 m). The contents of these metals in the reference areas were lower in the distance of 5m from the road (in the case of nickel and chromium – trice, copper – twice), while the contents of lead and cadmium were nearly identical (Tab. 2). These differences diminished with the growth of the distance from the road and the contents of the metals in the distance of from the road were even slightly lower than in the reference areas. The comparison of the mean concentration of metals in *Pleurozium schreberi* with the data presented by Mikos-Bielak and Tujaka [13] referring to the border check point in Dorohusk, allows for the statement that the contents of nickel and copper near the road Cracow – Zakopane made one third and a half of these values, respectively, while the values of zinc and lead were similar, and the values of cadmium were two times higher. The obtained results were also compared to the concentrations of metals in *Pleurozium schreberi* alongside eight Alpine roads in Austria [6]. The concentrations of chromium, lead, nickel and cadmium on the road Cracow – Zakopane were several times higher than in Austria (five times in the case of Cd and three times for Cr, Pb and Zn). Only concentrations of copper and zinc were similar. The comparison of metal concentration in moss *Pleurozium schreberi* in the direct vicinity of the road Cracow – Zakopane with the data for the area of Poland [14] indicate that at the road they were seven times higher in the case of chromium (13.1 μg/g and 1.8 μg/g d.w., respectively) in the case of nickel – five times (9.0 μg/g and 1.7 μg/g d.w.), and cadmium – three times higher (1.5 μg/g and 0.5 μg/g d.w.). The contents of copper, lead, and zinc were similar. It is worth mentioning that the contents of the latter did not change with the distance from the road, moreover, they were even slightly lower than in the reference areas. Sequences of declining mean concentrations of metals in moss *Pleurozium schreberi* came to the following form: Zn > Pb > Cr ≥ Cu ≥ Ni > Cd and were almost identical with the concentration sequences given by Grodzińska et al. [14] for Poland (Zn > Pb > Cu > Ni ≥ Cr > Cd). Higher contents of chromium in moss on the road Cracow – Zakopane than in other parts of Poland indicate that pollution with this element is connected with traffic, which is confirmed by the spatial distribution (decreased concentration) of chromium within the transects. Despite the fact that numerous authors recommend *Pleurozium schreberi* as one of the best phytoindicators [4–6, 15], using it in the studies of phytoindication in the vicinity of the Cracow – Zakopane route, causes certain difficulties due to the fact of the limited range in forests and open areas (pastures).

Leaves of dandelion *Taraxacum officinale* accumulated less heavy metals, compared to moss *Pleurozium schreberi* (Tab. 1). The content of chromium and lead in the direct vicinity of the road, compared to the reference areas were twice as high. The concentrations of metals in the samples taken at a distance of 100 m from the road, similarly as in the case of moss *Pleurozium schreberi,* were lower in the reference areas; the exception was lead (Tab. 2). The contents of chromium and lead indicated the decrease with the distance from the road, while such a rule has not been noticed in the case of other metals, moreover, the concentrations zinc and nickel, and in particular cadmium were higher in the reference areas. The contents of cadmium on the road Cracow – Zakopane are three times lower than the ones found by the roads of differentiated traffic intensity in the Pomerania – Kujawy region [16]. The contents of copper, zinc, and lead at a distance of 5 m and 10 m from the road, were similar to the lowest concentrations found in the industrial areas of the Upper Silesia [17]. The dandelion, because of its wide distribution is recommended as phyto-indicator [8, 18–20].

Two year needles of spruce *Picea abies* accumulated small quantities of metals, compared to moss *Pleurozium schreberi* and leaves of the dandelion *Taraxacum officinale* (Tab. 1), which complies with the literature data [7, 11]. The contents of metals in spruce are generally low and show little differentiation with the distance from the road. The concentrations of the metals in the samples taken at a distance of 100 m from the road, similarly like in the case of the moss *Pleurozium schreberi* and dandelion *Taraxacum officinale* were lower in the reference areas. Only the content of lead in the direct vicinity of the road compared to reference areas was twice as high. The contents of heavy metals in spruce found near "Zakopianka" were lower than in the Karkonosze National Park [11], in the Izer Mountains [21], and in the area of State Forests near Cracow [22]. Despite the fact that, among the tested plant species, the Norway spruce took the lowest amounts of heavy metals, it can be recommended as a good bioindicator of traffic pollution, in particular in the mountain regions of South Poland, where it is a dominant tree species. Decreasing sequences of mean metal concentrations in the danelion and Norway spruce had the same form: Zn > Cu > Ni > Pb > Cr > Cd, different than *Pleurozium schreberi.* Vascular plants, like moss *Pleurozium schreberi* took the highest amount of zinc, and the smallest of cadmium. The difference was the high content of copper, compared to *Pleurozium schreberi*. The content of lead in dandelion was several times lower than in moss, which could result from a shorter time of contact (a few months for the dandelion, about two years for the moss *Pleurozium schreberi*) of assimilating organs with traffic pollution.

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